THE FORMATION OF MONOVALENT INDIUM DURING ANODIC SOLUTION OF THE INDIUM ELECTRODE

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On the basis of results of studying the electrochemical behavior of an amalgam indium electrode [1], the hypothesis was advanced that the electrode process proceeds stagewise with the formation of indium ions of intermediate valencies:

$$In \rightleftharpoons In^{+} + e \tag{1a}$$

$$In^{+} \rightleftharpoons In^{2+} + e \tag{1b}$$

$$In^{2+} \rightarrow In^{3+} + e \tag{1c}$$

where the first two stages are equilibrium states, while the separation of the third electron (1c) is the limiting stage of the anode process. To justify this mechanism it is of major interest to detect directly the formation of In^{+} during the electrode process. If stage (1a) is actually an equilibrium state, then the concentration of In^{+} should be determined simply by the potential of the indium electrode according to the equation

$$\varphi = \varphi_0 + \frac{RT}{F} \ln [In^{+}] \tag{2}$$

and hence should increase with anodic polarization and decrease with cathodic polarization of the electrode. Moreover, further oxidation of the ions of monovalent indium forming during anodic polarization can take place not only on the electrode [reactions (1b) and (1c)], but also by interacting with components of the solution. The anode yield with respect to current (calculated for the formation of In^{3+} ions as the final product of the electrode process) should hereby exceed 100% or, what is the same thing, the "effective initial valence" n_i [2, 3] of the indium ions formed should be less than 3. Inasmuch as the quantity n_i is determined by the ratio of the rates of oxidation of In^{+} ions on the electrode and in solution, it should depend on the potential of the electrode [3] and also on the concentration of that component of the solution which participates in the reaction of oxidizing In^{+} ions. During the anodic solution of indium amalgam ($2 \cdot 10^{-3}$ to 0.9 M) in perchlorate solutions the quantity n_i was found equal to 3 and did not change with change in the potential of the amalgam and the acidity of the solution [1]. However, with anodes of solid indium in water-free acetic acid [2], in liquid ammonia [4], and also in solutions of $Mg(ClO_4)_2 + C_2H_5OH$ [5] magnitudes of n_i considerably less than 3 were observed. During anode solution of indium in subacidic, aqueous sulfate solutions the yield with respect to current somewhat exceeds 100% [6, 7]. It has also been shown [6, 8, 9] that In^{+} ions are formed when metallic indium comes in contact with a solution of a trivalent indium salt; the equilibrium concentration of these ions reaches 1% at a pH = 2. It may be supposed that the difference in the behavior of the amalgam and solid electrode is related to the fact that anodic oxidation of In^{+} ions on the amalgam electrode proceeds considerably faster than on solid indium [10]; consequently, in the latter case it is easier to detect the process of oxidation of In^{+} ions in the solution and also the change in their concentration with the potential of the indium electrode by using an auxiliary indicator electrode.

The object of the present work was to detect during the electrode process the formation of indium ions of intermediate valency on the indium electrode in order to verify directly the stepwise couse of this process.

The tests were conducted in the cell previously described having a rotating indium electrode (460 rpm) [11] at 20° in an atmosphere of purified nitrogen in solutions of $In(ClO_4)_3 + HClO_4$ ($3 \cdot 10^{-3}$ to 1 M) with the addition of

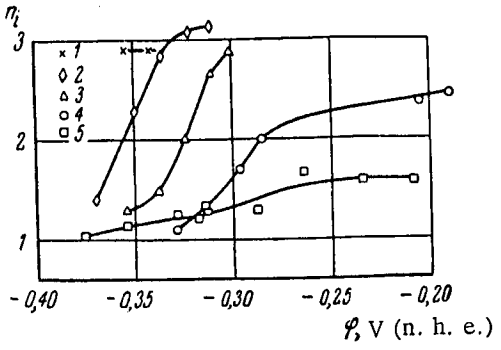

Fig. 1. Dependence of the effective valence n_i on potential at various $HClO_4$ concentrations. 1) $3 \cdot 10^{-3}$ M; 2) $1 \cdot 10^{-2}$ M; 3) $5 \cdot 10^{-2}$ M; 4) 0.2 M; 5) 1 M.

$NaClO_4$ to preserve constant ionic strength ($\mu = 3$). In order to determine the effective initial valence of dissolving indium n_i*, the electrode was seeded with the radioactive isotope In^{114}, and the increase in radioactivity of the solution during anode polarization of the electrode at a given current density was recorded with an instrument for the continuous measurement of radioactivity [12]. The current densities applied ($3 \cdot 10^{-5}$-$6.6 \cdot 10^{-2}$ A/cm^2) were such that passivation of the electrode in the given solution should not yet occur and the potential should not change appreciably with time. Before anode polarization was begun the rate of self-solution of the indium electrode was measured, and a corresponding correction was made in the results obtained. Computation of n_i was carried out according to the usual formula

$$n_i = \frac{A \cdot Q}{p \cdot F}, \tag{3}$$

where A is the atomic weight of indium, Q the amount of electricity passed (G), and p is the amount of metal dissolved (g); here

$$Q = i \cdot S \cdot \Delta t,$$

where i is the current density (A/cm^2), S the electrode area (cm^2), and Δt the duration of the test (sec), while

$$p = \frac{p_0 \cdot \Delta I \cdot v_1}{I_0 \cdot v_0}$$

I_0 and v_0 being the radioactivity and volume of the calibration solution, P_0 the amount of indium in this solution, ΔI the increase in radioactivity of the solution during the time of the test, and v_i the volume of the solution in the cell. As a result we obtain from (3) the following formula for computing n_i from the data of the radiochemical measurements:

$$n_i = \frac{A \cdot i \cdot S \cdot \Delta t \cdot I_0 \cdot v_0}{p_0 \cdot \Delta I \cdot v_1 \cdot F}. \tag{4}$$

The dependence of n_i on the potential of the electrode at various $HClO_4$ concentrations is shown in Fig. 1. At a given $HClO_4$ concentration n_i increases as the potential moves toward the positive side, and at a fixed potential it decreases with increase in the $HClO_4$ concentration. Such a dependence of n_i on the potential and the acidity can be explained if it is supposed that anodic solution of indium proceeds stagewise with the formation of unstable In^+ ions which are oxidized to stable In^{3+} ions by two parallel reactions: either by interaction in the solution with H^+ ions (this is indicated by the dependence of n_i on the concentration of $HClO_4$):

$$In^+ + 2H^+ = In^{3+} + H_2, \tag{5}$$

or by direct oxidation on the electrode (this is indicated by the dependence of n_i on the potential)

$$In^+ \rightarrow In^{3+} + 2e. \tag{6}$$

The rates of these reactions are expressed by the equations

$$v_1 = k_1[In^+][H^+]^2,$$
$$v_2 = k_2[In^+]e^{\beta\varphi F/RT}.$$

The quantity n_i should be the greater the higher the rate of electrochemical oxidation of In^+ ions, i.e., the larger the ratio

$$\frac{v_2}{v_1} = \frac{k_2 e^{\beta\varphi F/RT}}{k_1[H^+]^2}, \tag{7}$$

*The tests to determine n_i were conducted in the absence of $In(ClO_4)_3$.

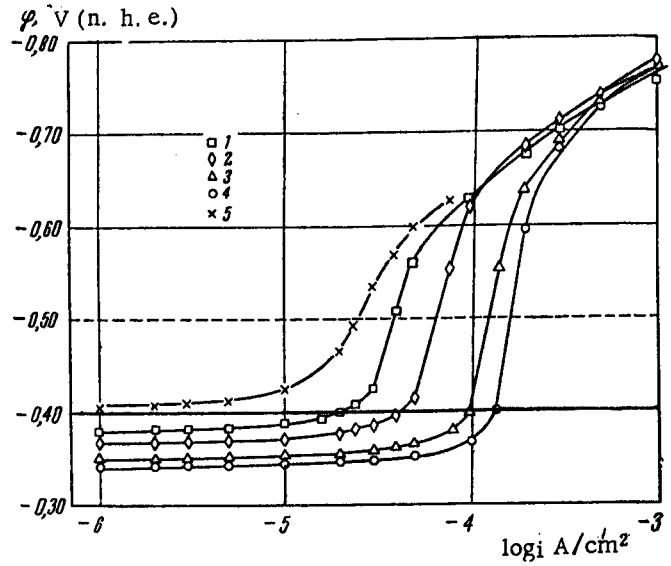

Fig. 2. Cathode polarization curves for a solution of $2 \cdot 10^{-3}$ M $In(ClO_4)_3$ + $5 \cdot 10^{-2}$ M $HClO_4$ taken after imposing anodic impulses ($i_a = 5 \cdot 10^{-4}$ A/cm²) of the following durations: 1) 30; 2) 60; 3) 120; 4) 180 sec; 5) initial nonstationary curve.

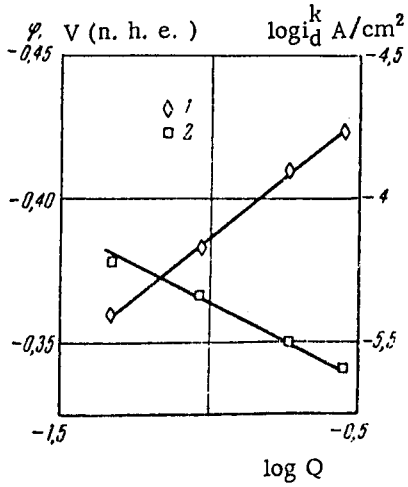

Fig. 3. Dependence of the rate of the cathode process at $\varphi = -0.50$ V (1) and the equilibrium potential (2) of the main electrode after shutting off the current on the amount of electricity passed during the previous anodic polarization.

which increases when the electrode is moved toward the positive side* and when the acidity is reduced; the quantity n_i hereby tends to the limit $n_i = 3$ (when $v_2 \gg v_1$). This agrees wells with the curves shown in Fig. 1. According to equation (7), the lowest values of n_i should be expected at low current densities when the potential of the electrode is near the equilibrium value and in the most acidic solutions. Under these conditions it is actually possible to observe experimentally values of n_i close to 1 (Fig. 1); moreover, during anodic polarization of indium in 1 N $HClO_4$ observable evolution of hydrogen occurs in the anode space which is related to the oxidation of In^+ ions according to reaction (5). Apparently, monovalent indium can also be oxidized in solution by ClO_4^- ions; this is indicated by the formation of Cl^- ions in the anolyte, but the rate of this process is considerably less than the rate of reaction (5)†.

The appearance in the solution during anodic polarization of indium particles which possess a high reactivity is indicated by the cathode polarization curves taken rapidly on the indium electrode after preliminary anode polarization (Fig. 2). The rate of the cathode process in this case rises rapidly as the duration of the anodic impulse is increased. Figure 3 shows the dependence of the rate of the cathode process i_d^k at constant potential on the amount of electricity Q passed previously in the anode direction which was

*The conclusion of the dependence of n_i on potential was first made and experimentally founded in the case of the anodic solution of magnesium [3].

†As has been shown by the study of the kinetics of oxidation of In^+ ions in solution [10], this process actually proceeds mainly be reaction (5) and only at low acidities is an appreciable part of monovalent indium apparently oxidized by other components of the solution, in particular by ClO_4^- ions. Moreover, the total concentration of ClO_4^- ions in our experiments was constant (3M); therefore, if monovalent indium were oxidized mainly by ClO_4^- ions, then the strong dependence of n_i on acidity which we observed could not be explained (Fig. 1).

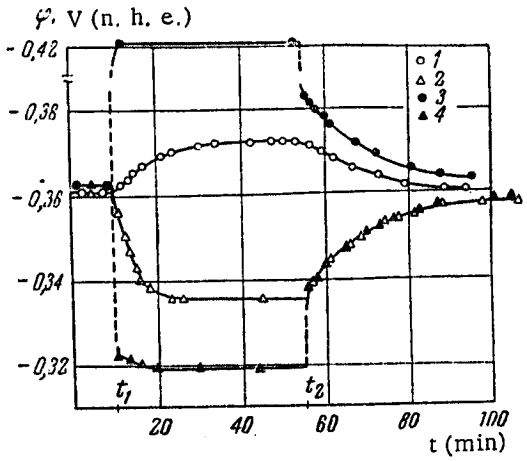

Fig. 4. Time variation of the potential of the indicator (1, 2) and main (3, 4) indium electrodes in a solution of 0.01 M $In(ClO_4)_3$ + 0.01 M $HClO_4$ with (t_1) and without (t_2) anodic ($5 \cdot 10^{-4}$ A/cm^2) and cathodic polarization ($1 \cdot 10^{-4}$ A/cm^2) on the main electrode.

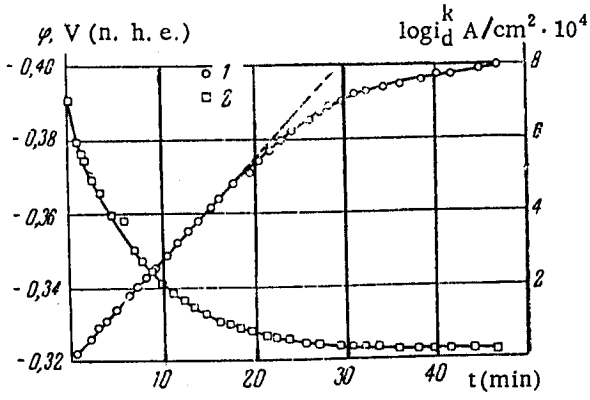

Fig. 5. Dependence of the potential of the indicator electrode (1) and the current density on the main electrode (2) on time during cathode polarization of the main electrode at φ = -0.5 V in a solution of $3.5 \cdot 10^{-3}$ M $In(ClO_4)_3$ + 0.05 M $HClO_4$ after anodic impulse ($i = 2 \cdot 10^{-3}$ A/cm^2) for a period of 10 min.

found from this graph. The slope of the line (log i_d^k, log Q) is close to 1, and hence the rate of the cathode process is proportional to Q. After three-minute anodic polarization the rate of the process increased by more than six times, while the equilibrium potential of the electrode measured directly after cessation of anodic polarization (Curve 2, Fig. 3) moved to the positive side by more than 60 mV. Moreover, the total concentration of indium in the solution (taking into account the In^{3+} ions present in the solution before anode polarization) rose by not more than 5%. Hence, the effect of the increase of cathode current cannot be explained simply by the rise in the total amount of indium in the solution*; evidently, it is mainly those particles of indium which enter the solution during the time of the anodic impulse which participate in the cathode process. The results described indicate that the limiting cathode current is proportional to the concentration of these particles. The rate of their discharge is limited by diffusion, as is shown by a simple calculation†.

To determine the conditions of accumulation in the solution of reactive indium particles and to identify them, experiments were conducted with an auxiliary indicator electrode which consisted of a platinum wire covered with the very same galvanic deposit of indium as the main electrode. Together with cruves of the variation in potential of the main indium electrode in a solution of 0.01 n $In(ClO_4)_3$ during polarization and after shutting off the current, Fig. 4 shows curves of the variation of potential of the indicator electrode in the same solution not subjected to polarization which were taken at the same time. During anodic solution of the main electrode the potential of the indicator electrode is gradually displaced toward the positive side and approximately after 10 min reaches a certain stationary value. After cessation of polarization of the main electrode the potentials of both electrodes assume the same values and gradually return the initial value of equilibrium potential. Analogous effects are observed during cathode polarization.

These experiments indicate that displacements of the equilibrium potential of the main indium electrode which remain after cessation of anode polarization (curve 2, Fig. 3)

*It has previously been shown [11] that the rate of discharge of In^{3+} ions in 0.05 M $HClO_4$ is considerably lower than the limiting diffusion current and is limited by previous chemical reactions in the solution.

†In the calculation it was assumed that in the cathode process participate only In^+ ions forming during the anodic impulse. The concentration of In^+ ions was computed from Q taking into account the quantity n_i for the given potential and acidity (curve 3, Fig. 1); the thickness of the diffusion layer δ for this process was estimated from the (log i_d^k, log Q) dependence (the coefficient of diffusion of In^+ ions was taken equal to the coefficient of diffusion of Tl^+). The value $\delta = 1.6 \cdot 10^{-3}$ cm thus found agrees satisfactorily with the value $\delta = 2.9 \cdot 10^{-3}$ cm formerly obtained from the limiting current for discharge of copper ions under the same mixing regime [11]; this is indicative of the diffusion nature of the limiting cathode current.

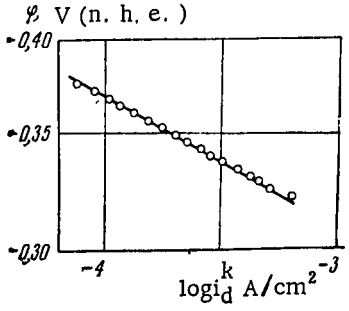

Fig. 6. Dependence of the potential of the indicator electrode on the density of the limiting cathode current on the main electrode computed from the data of Fig. 5.

are not related to the change in the condition of its surface, but are rather occasioned by an increase in the concentration of the potential-determining particles of indium in the solution. The relative changes in the concentration of In^{3+} ions during the time of polarization is not only too small to cause the observed changes in the potentials of the main and indicator electrodes (cf. above), but they also could not explain the subsequent gradual return of the potentials to the stationary value. These effects, and also the character of the change of potential of the indicator electrode during cathode polarization, are easily explained if it is assumed that the potential-determining particles, the concentration of which in the solution rises during anodic polarization and drops during cathodic polarization, are ions of monovalent indium.* In this case the potential of the indicator electrode should uniquely determine the concentration of In^+ ions in the solution according to equation (2). To check this conclusion, after preliminary anodic polarization a curve of limiting cathode current vs. time (at $\varphi = -0.5$) was taken on the main electrode and a curve of potential vs. time (Fig. 5) was taken on the indicator electrode in the same solution. Inasmuch as the limiting cathode current i_d^k is proportional to the concentration of indium ions present in the solution at the given moment (of the number entering the solution during the anodic impulse) which, according to our hypothesis, are In^+ ions, equation (2) may in this case be written in the form

$$\varphi = \varphi_0 + \frac{2.3RT}{F} \log i_d^k + \text{const.} \qquad (8)$$

From the experimental data given in Fig. 5 the (φ, $\log i_d^k$) dependence was calculated (Fig. 6) which is expressed by a straight line with a coefficient of slope of 0.057 V†. The good agreement of this coefficient of slope with the theoretical value corresponding to equation (8) convincingly demonstrates that the ions determining the potential of the indicator electrode which form during the anodic impulse and are mainly discharged during subsequent cathode polarization are ions of monovalent indium. The potential of the main indium electrode after cessation of anode polarization coincides with the potential of the indicator electrode (Fig. 4), and hence the potential of the main indium electrode can also serve as a measure of concentration of the In^+ ions entering the solution during the time of the anodic impulse.

The results presented of the experiments for determining the effective initial valence n_i of anodic solution of indium and also for detecting directly the presence of ions of monovalent indium in solution using an indicator electrode indicate that the anodic solution of indium proceeds stagewise with the intermediate formation of ions of monovalent indium, the further oxidation of which can occur not only on the electrode but in solution as well. The low values of n_i during anodic solution of indium cannot be explained by a negative differential effect, i.e. by an increase in the self-solution of the anode due to the decrease of overcharged hydrogen on it, as has been done by several authors to explain the low values of n_i on aluminum and magnesium anodes [13, 14], since the effects of change in potential of the indicator electrode during anode polarization which we found would hereby remain unexplained.

The low values of n_i also cannot be explained by the accumulation of In^+ ions in solution during the initial period of anodic polarization and their subsequent oxidation on the electrode alone according to reaction (6). Actually, in this case the values of n_i should gradually increase in time during anode polarization and tend to $n_i = 3$, but our data indicate that the values of n_i remain practically unchanged in time even during long anodic polarization (30-40 min) when a stationary concentration of In^+ ions has already been achieved in the solution (this occurs already within 10-15 min, as is evident from the curves of change in potential of the indicator electrode in time during anodic polarization, Fig. 4).

*The gradual return of the potentials of both electrodes to the initial equilibrium potential after cessation of anodic polarization is related to the oxidation of In^+ ions in solution according to reaction (5), while the slow displacement of these potentials after cessation of cathodic polarization is occasioned apparently by the regeneration of In^+ ions by the occurrence on the surface of the electrodes of the combined reactions $In \rightarrow In^+ + e$ and $In^{3+} + 2e \rightarrow In^+$ [10].

†The calculation was made in the following manner: the quantity i_d^k corresponding to the experimental value of the potential measured at a given instant of time was determined for various values of the time t from curve 2 (Fig. 5).

In conclusion it should be noted that, in distinction to the dilute amalgams mentioned at the beginning of the article [1], during anodic solution of very concentrated indium amalgams (20-60%) in 0.1-3 M $HClO_4$ and in other acids reduced values n_i of the effective valence were also observed which rose to 3 as current density increased [15]. Apparently, with respect to electrochemical properties the concentrated amalgams are closer to solid indium than to the dilute amalgams. Thus, for example, with rising concentration of the amalgams its equilibrium potential and anodic polarization curve move toward the negative side; this must lead to a decrease in the rate of electrochemical oxidation of In^+ ions, and the quantity n_i should decrease hereby, according to equation (7) In addition, the potential of zero charge of the concentrated indium amalgams is strongly displaced to the negative side [16]. Hence, the process of electrochemical oxidation of In^+ ions should in this case occur on a positively charged electrode surface and not on a surface with negative charge as in the case of dilute amalgams; this may also cause retardation of the oxidation process.

We wish to express our deep thanks to Ya. M. Kolotyrkin for his valuable advice in discussing the results of this work.

CONCLUSIONS

It has been established that the anodic solution of metallic indium in perchloric acid solutions proceeds with the formation of ions of monovalent indium which subsequently either enter into chemical reaction in solution or are oxidized to ions of trivalent indium directly on the electrode, whereby the rate of this reaction depends on the potential.

The initial effective valence of indium entering the solution varies from 1 to 3 depending on the ratio of the rates of chemical reaction of ions of monovalent indium in the solution and electrochemical oxidation on the electrode.

The formation of ions of monovalent indium during anodic polarization of the indium electrode has been demonstrated directly with the help of an indicator electrode.

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